Research Brief for
DOE/IHEA Process Heating Materials Forum

Research Title: Modeling of Thermo - Chemical - Kinetic reactions between Gas – Liquid – Glass - Metal in Industrial Process Heating Environment

Industry Need: The material selection for process heating equipment must optimize on high temperature properties including tensile, compressive, shear, creep and fatigue. In addition, they are expected to withstand wear and oxidation and as well as corrosion resistance in different process environments that may have liquid metal, steam, hydrogen and high-carbon activity. To evaluate wide range of high temperature metals and refractories it is desirable to describe the response of materials to process heating environments through computational thermodynamic and kinetic models.

Existing Research: In ongoing research, we evaluated the phase stability of high temperature metals such as austenitic Ni-base, Ni_3Al intermetallics, Fe-Al Intermetallics and ferritic Fe-Cr-Al alloys in ethylene cracking environment. Using computational thermodynamics, we have described the oxide formation in oxidizing atmosphere, carbide formation during carburization conditions [see Fig. 1] and sulfide formation in the sulfur-rich environments. Using these results, we have designed new high temperature metals. Based on the coupled thermodynamic and kinetic models there is a potential to describe the reactions that occur in high-temperature metals for any process environments.

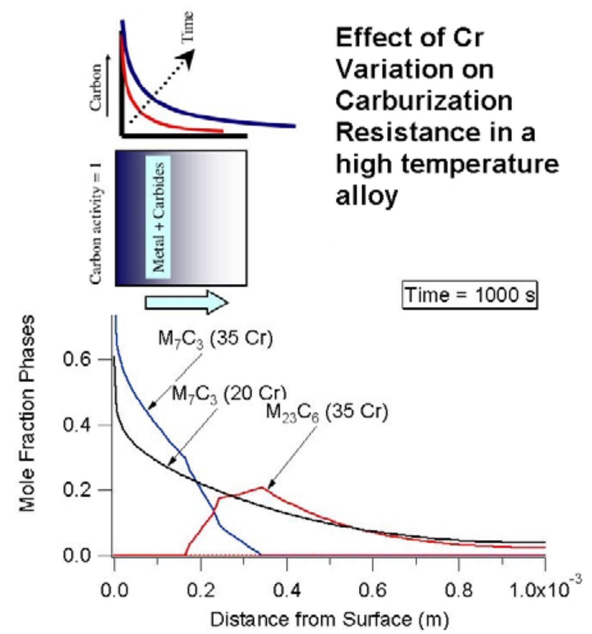

Fig. 1 Predicted variation of carbide mole fraction as a function of distance in a Fe-Al alloy with different Cr-concentrations at 1000°C.

Similarly, we have developed thermodynamic models to describe phase stability in refractories and glasses. The approach is based on the modified associate species model, which has proven highly accurate for reproducing phase relations, liquidus surfaces, vapor pressures, and chemical activities of relatively simple glasses. It treats the melt and glass as an ideal solution of constituent species, and thus easily accommodates large numbers of elements. The typical nonideality of oxide solutions is treated by including in the solution not only the end-member simple oxides, but as necessary, binary and ternary oxides liquid species. These are tested against known phase equilibria, which are very sensitive to thermodynamic values of the constituents, and to be accurate must reproduce important segments of the phase diagrams.

Proposed Activity: We propose to develop comprehensive coupled thermodynamic-kinetic model to describe thermo-chemical-kinetic reactions between gas, liquid, glass, and metal with the Industrial process-heating environment. The research will be divided in tow sub categories: (1) describing the stability of high temperature metals and (2) stability of refractories including glasses.

Metal Stability Research: A high-temperature metal is usually based on strengthening the alloy by adding alloying elements to provide solid solution hardening or to enhance precipitate formation. For example, in a nickel base superalloy, γ' precipitates based on Ni_3Al intermetallic crystal structure form within the matrix and strengthen. However, all these solid solution elements on exposure to process heating environment will react to form their respective oxides, carbides, sulfides, nitrides and hydrides based on the thermodynamic activity of oxygen, carbon, sulfur, nitrogen and hydrogen. Depending upon thermodynamic driving force and diffusion of elements, there will be competition between oxides, carbides, sulfides, nitrides and hydride formation. Therefore, we propose to develop a simultaneous transformation kinetic model that will describe this competition based on the process heating environment and the metal composition. The predictions will be compared with experimental information that will be provided by the participating industrial partner.

Refractory Stability Research: Refractories can range from single-phase materials to complex mixtures of crystalline phases and amorphous phase(s). These latter systems are currently not described by any thermochemical models. For example, glassy grain boundary phases are often the site of corrosive attack and the source of failure. Yet there are no models for the chemical interactions of the glassy phases with corrodents. The proposed work develops models of the glass grain-boundary phases along with assessed thermochemical properties of the crystalline phases of the refractory. This would allow assembly of a global model of the refractory that would form the basis for assessing the effect of potential corrodents. Such approaches would also be useful for other materials, particularly non-metal, high temperature materials, where complex oxide and other phases are created. In this proposed research, some adjustment of the thermodynamic values of the binary or ternary oxide liquids will be necessary, and thus they are fit to obtain an accurate model. The "modification" of the associate species model involves the treatment of immiscibility, which requires the use of a solution model with positive interaction energies. The global model is finally created by including the various species of the subsystems into single solid solution. The result is an accurate representation of the behavior of a complex, multi-component system.

Lead Scientists:

Dr. Theodore M. Besmann
Head, Surface Processing & Mechanics Group
M&C Division, Oak Ridge National Laboratory,
1 Bethel Valley Road, P.O. Box 2008, Oak Ridge, TN 37831-6063
Tel: (865) 574-6852; Email: tmb@ornl.gov
http://www.ms.ornl.gov/sections/mpst/SPM/spmframes.htm

Dr. Sudarsanam S. Babu
Senior R&D Staff, Materials Joining Group
M&C Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6096
Tel: (865) 574-4806; Email: babuss@ornl.gov
http://mjndeweb.ms.ornl.gov/Babu/